Study of oxidation of Propane 1,2-diol by IQBC in acetic acid medium: Thermodynamically approach

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Abstract

In Proposed study work we explored the kinetic and mechanism of oxidation of Propane 1,2-diol by Isoquinolium bromochromate in aqueous acetic acid medium because it is an ecofriendly, cheap, non-hazardous and easily synthesized in chemical laboratories and available in market. Proposed study work was carried out at 298^0 K, we have analyzed oxidation of Propane 1,2-diol by isoquinolium bromochromate in aqueous acetic acid medium. Reaction follows first order kinetics at low concentration of Propane 1,2-diol with trend towards zero order at its higher concentration with respect Isoquinolium bromochromate and the reaction is acid catalyzed. In order to study the effect of catalyst ions were chosen as CuSO4 and MnSO4 were taken as the cat ions sources of Cu^{++} and Mn^{++} ions. The effects of these ions were studied by adding varying concentration of $Cu^{++}$and Mn^{++} to the reaction mixtures, keeping the concentration of substrate, oxidant and composition of acetic acid water and temperature constant.

Key words: Oxidant, reaction, mechanism, liner and reagent.

Introduction:

In the recent years, studies of oxidation of various organic compounds by heteropoly acids and Polyoxometalates especially those with Keggin-type structure under homogeneous and heterogeneous reaction conditions[1-9] have attracted considerable attention of the researchers. Chemical kinetics[10] is a branch of chemistry, which deals, with the measurement of the rates of chemical reaction. An ideal theory of chemical kinetics would start with the time dependent equation which could be solved to predict the rates of such simple physical and

chemical processes as changes in the energy state of a molecule and energy transfer reactions in which a net chemical changes occurs but energy is transferred between molecules. Livingston[11] called the special attention of signifying in field of reaction mechanism as "No reaction mechanism can be considered to be more than a temporary working hypothesis until its supported by kinetic data".

A number of new chromium containing compounds[12] like pyridinum bromochromate[13], quinolinium chlorochromate[14] 2,2-bipyridinium chlorochromate[15], pyridinium fluorochromate[16], quinolinium fluorochromate[17], quinolinium bromochromate[18], quinolinium dichromate[19], pyridinium fluorochromate[20], imadazolium fluorochromate[18] have been used to study the kinetics and mechanism of oxidation of various organic compounds.

The most classical and versatile reagents, however, are periodic acid and lead tetra acetate[22] , between these two reagents, most carbon-carbon bond fission of α-diols, α-diones, α-keto and hydroxy acids and α-hydroxy ketones can be carried out selectively under mild conditions and in good yield. The two reagents are complementary, since periodic acid is best used in water and lead tetra acetate in organic solvents.

Materials and method

The kinetic study for the oxidation of propane 1,2-diol with IQBC in aqueous acetic acid medium have been carried out. The solutions of propane 1,2-diol (B.D.H.) have been prepared in requisite amount of acetic acid water mixture of appropriate compositions. Other chemicals used were of standard grade. To prevent photochemical effect the freshly prepared solution of Isoquinolium bromochromate was stored in an amber color bottle. The purity of reagent was confirmed by spectraland elemental analysis.

Isoquinolinium bromochromate (Loc cited)[9] was prepared by the following method : chromium trioxide (10 g, 0.1 mol) was dissolved in water (15 ml) and cooled to 0° C. To this solution was added hydrobromic acid (17 ml, 48%) slowly with vigorous stirring, then isoquinoline (13 ml, 0.1 mol) was added drop wise during 10 min. The reaction mixture was cooled for 2-3 hours and filtered. The resulting yellow orange needles were dried and

recrystallised. The purity of reagent was confirmed by spectral and elemental analysis. Infrared spectrum (KBr) gave bands at 945, 868, 767 and 621 cm^{-1} characteristics of dichromate ion. The reagent had a melting point of 105-106° C and a molecular formula of $C_9H_7N^+HCrO_3^-$ Br (iso). Starch solution has been used as an indicator for iodometric estimation. Its solution was prepared according to method given in vogel's books. The solution of other chemicals used was prepared either by direct weighing or standardizing them by established methods

Experimental

Preliminary experiments for the oxidation of propane 1,2-diol with IQBC were conducted to choose the appropriate conditions of concentration of the reactant and temperature so that the oxidation could proceed with measurable rate. It has been observed that in presence of minerals acids the oxidation of these substrates proceeds at a very slow rate[23]. Hence the study was switched on at slightly higher temperature. In each set of reaction of substrate was taken in large excess over the concentration of oxidant. The amount of unreacted IQBC was estimated iodometrically[24-26] with the standard solution of sodium thiosulphate using starch as an indicator. The stoichiometry[27-29] of each reaction understudy was determined under experimental conditions. The formation of free radicals[24,25] if any during the course of reaction was identified using the solution or acrylonitrile (monomer) by trapping method.

Result and Discussion

The plot of K_1 VS $[H_2SO_4]$ and K_1 VS log $[H^+]$ fig. I is linear with unit slope exhibiting first order with respect to H_2SO_4 for propane 1,2-diol hence the reaction shows first-order kinetics with respect to IQBC. Experimental work present in table -I for propane 1,2-diol under investigation. The reactions are acid catalyzed.

H_2CrO_4 have been reported as the active species. The stoichiometric studies of propane 1,2-diol - Isoquinolium bromochromate system at experimental temperature have been investigated separately. It was found that for each mol of substrate 1 mole of oxidant is consumed.

Waters et al.[30] (1953) and Hinshelwood[31] have also been reported such a consumption of oxidant in the oxidation of propane 1,2-diol with alkaline $KMnO_4$ and Ce(IV).The oxidation products corresponding propane 1,2-diol was identified for each oxidation as dione[32] qualitatively and chromatographically and also by existing methods.

The aldehydes and ketones were also reported by various authors and co-workers in their previous works by Carrying similar oxidation of propane 1,2-diol with variety of oxidants such as: NCSA[33], SeO_2[34], $KMnO_4$[35], Mn(III)[36], bromanine-T[37] , but most appropriate and authentic methods confirmed diones as the main oxidation products.

Table - 1

Dependence of rate on the concentration of Sulphuric acid

10^2 × [propane 1,2-diol] (mol dm^{-3}) = 2.50;

10^2 × [substrate] (mol dm^{-3}) = 2.50;

HOAc-H_2O % (v/v) = 30;

Temperature^o K = 298

S.N.	$[H^+] \times 10^2$ (mol dm^{-3})	Propane 1,2-diol
1.	0.50	6.14
2.	1.00	6.32
3.	1.25	6.94
4.	1.50	7.31
5.	2.00	8.01

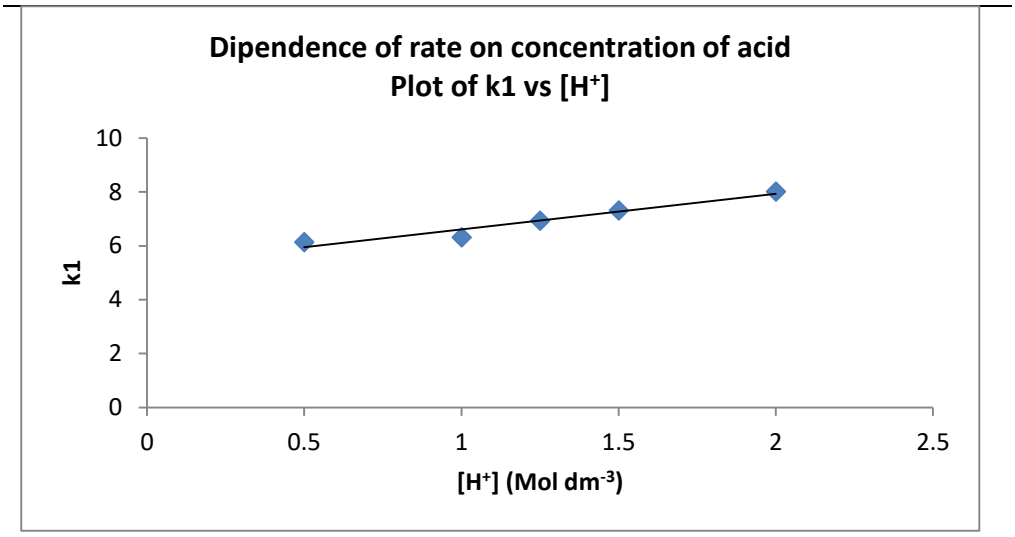
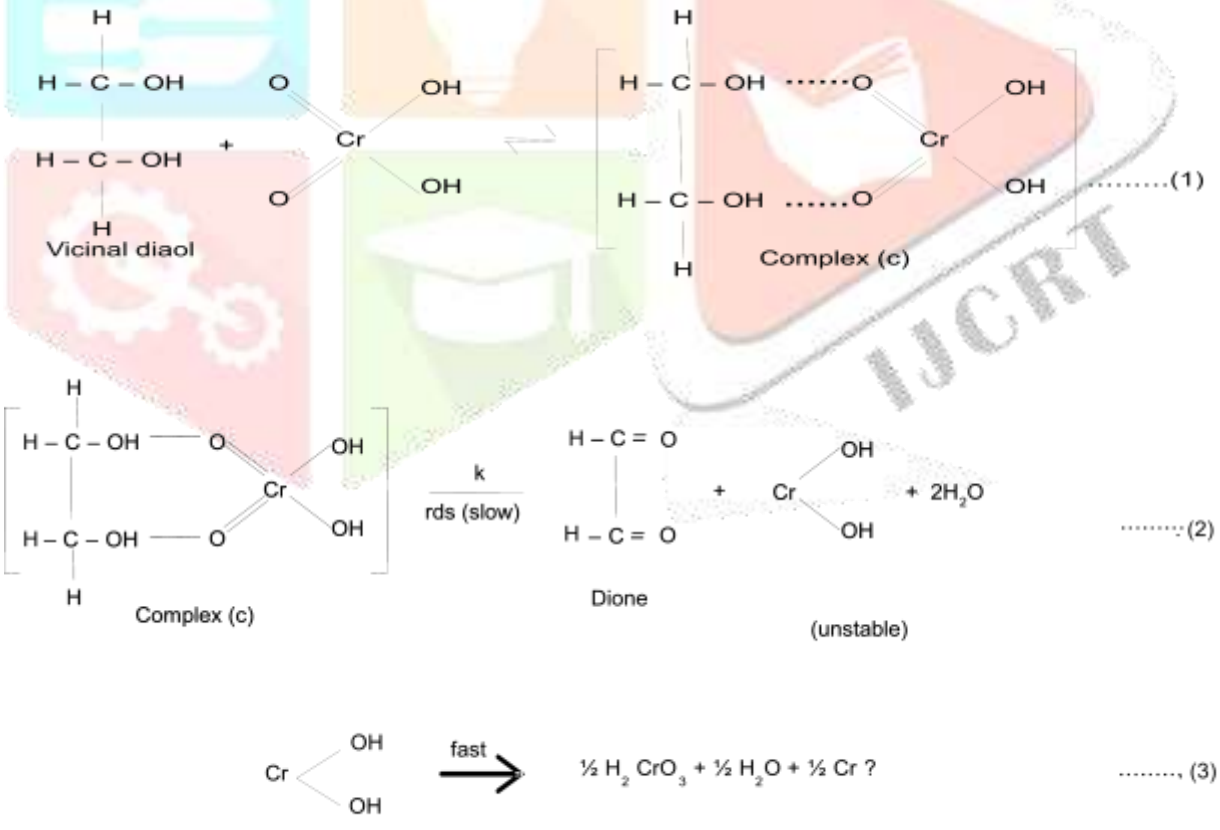


Fig I

Mechanism

Probable mechanism of oxidation of propane 1,2-diol by isoquinolium bromechromate:



As per experimental study reaction velocity show first-order kinetics at low concentration of propane 1,2-diol while turns to zero order at its higher concentration. That is

indicating for the complex formation with oxidant, as was observed by Michaelis and Menton[38], in enzyme catalyzed reaction. Considering these facts a probable mechanism for the oxidation of propane 1,2-diol with Isoquinolium bromochromate could be proposed as per following schemes, using H_2CrO_4 reacting species.

The rate law was derived as:

$$k_{obs}=\frac{\text{Rate}}{[Propane\ 1,2-diol]T}=\frac{\text{K1K2k[S][H}^+\text{]}}{[IQ]K1+K1K2[S]}$$

Where,

IQ=Isoquinoline, [S]=Substrate

Conclusion

1. Kinetic studies employing IQBC as an oxidant and allied aspects of its reactions lead us to conclude that the activity of IQBC is much limited and needs to be explored in a broad way. It possesses vital potentiality and displays interesting behaviours at moderate condition of temperature.
2. The study will certainly enlighten the future workers in carrying out researches of great value contribution and information through kinetic study will enrich chemical literature to a great extents.
3. It use can be extended in analytical, applied chemistry and in separation/ identification of organic compound.

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